

Chemical Factors Affecting Insolubles Formation In Shale-Derived Diesel Fuel

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Introduction

Deterioration in fuel quality with time has been a continuing problem in the utilization of middle distillate fuels. Diesel fuel instability is usually defined by the formation of insoluble sediments and gums and by the accumulation of hydroperoxides. Recent studies into the mechanisms of storage instability with middle distillate fuels have indicated that the presence of polar materials, particularly nitrogen heterocycles, can be detrimental to stability (1-4). In particular, nitrogen containing aromatics (pyrroles, pyridines, indoles, etc.) appear to be very harmful. Nitrogen heterocyclic compounds which commonly occur in middle distillate fuels include alkylated pyridines, quinolines, tetrahydroquinolines, indoles, pyrroles and carbazoles. Correlation of model dopant studies with results obtained with actual unstable fuels has indicated that the autoxidation processes are usually not isolated reactions but are sensitive to the presence of other fuel constituents. (1) Little is known about the chemical mechanisms of such interactive effects in fuel instability and possible explanations include acid/base catalysis of oxidation.

In our effort to define the stability of shale-derived diesel fuel, we have conducted gravimetric accelerated storage stability tests at 43 and 80°C using three model nitrogen compounds, 2-methylpyridine, 2,6-dimethylquinoline and dodecahydrocarbazole, as dopants in an otherwise stable shale diesel fuel. Also, information about potential interactive effects has been defined for these three model nitrogen compounds in the stable fuel in the presence of a second model dopant (a hydroperoxide, organic acid or base).

Experimental

Storage Test Techniques

The accelerated storage stability test method used has been described in detail (5). In summary, 300 ml samples of filtered fuel (doped and undoped) were stressed in the dark in 500 ml screw-cap borosilicate Erlenmeyer flasks with teflon-lined caps. All samples were run in duplicate or triplicate and appropriate blank flask/filter holder corrections were applied. Vented tests were accomplished by using modified screw caps which were drilled to hold 6 mm glass tubing (with glass wool plugs). Both filterable and adherent insolubles values were determined after

stress and these measured quantities were summed to obtain total insolubles, the values reported in the text and Tables. Hydroperoxide values were determined in stressed fuel samples following filtration through glass fiber filter paper by iodometric titrations. (ASTM D-1583-60)

Base Fuel

The base fuel was a diesel fuel marine (DFM) refined from Paraho crude shale oil by SOHIO. This fuel was produced in the Navy's Shale-II demonstration and is well characterized (5-8). It was available with (sample "D-11") and without (sample "D-1") antioxidant added. The antioxidant, 2,4-dimethyl-6-*t*-butylphenol (AO-30), was originally present at the 24 mg/liter level in fuel D-11. No other additives were present in either sample. All compounds used as dopants were pure by NMR, capillary GC, and/or melting point.

Results and Discussion

Accelerated storage stability tests were conducted at 43° and 80°C for periods of time ranging from 7 to 141 days, respectively, using three model nitrogen compounds as dopants in a stable shale diesel fuel. The three model compounds, 2-methylpyridine (2-MP), 2,6-dimethylquinoline (2, 6-DMQ) and dodecahydrocarbazole (DDC) were added to samples D-1 or D-11 at concentrations of 0, 45, 135, 270 and 450 ppm N(w/v), and vented trials were also conducted at 45 and 450 ppm.

Results obtained from the gravimetric test matrix indicated that 2-MP and 2, 6-dimethylquinoline were inactive in sediment promotion at all temperatures, times and concentrations employed. In all instances, the total insolubles formed never exceeded 2 mg/100 ml or 1 mg/100 ml when 2-MP or the quinoline, respectively, were added.

Large amounts of insoluble sediments were formed when DDC was added as a dopant to the shale DFM as shown in Table I. For the 43°C tests, venting of the test flasks considerably reduced the yield of solids at both 45 and 450 ppm N(w/v) of added DDC. The reaction order was less than 1.0 for both temperatures used. Longer stress times did not increase total insolubles under some stress conditions.

Autoxidation of 2-MP, 2,6-DMQ and DDC in the Presence of *t*-Butylhydroperoxide (TBHP)

The initial interaction study involved the addition of a model nitrogen compound to fuel D-11 together with a hydroperoxide as co-dopant. The hydroperoxide selected was *t*-butylhydroperoxide since it is available commercially in high purity. The goal of the experiments was to survey the importance of the accumulation of hydroperoxides in a complex fuel in influencing the formation of insolubles during stress when a particular class of nitrogen heterocycles is present.

Accelerated storage stability tests employing 2-MP, 2,6-DMQ and DDC along with TBHP as co-dopants in fuel D-11 were run at 80°C for 14 days. The gravimetric results for tests run with 2-MP and TBHP, summarized in Table 2, indicated that a slight positive interaction existed under all conditions examined. The total amount of insolubles never exceeded 2.5 mg/100 ml even when the H1 TBHP concentration was used. The concentration matrix which was studied used 2-MP at two levels: Lo 2-MP = 135 ppm N (w/v), equivalent to $9.64 \times 10^{-3}M$; and H1 2-MP = 450 ppm N ($3.21 \times 10^{-2}M$). The levels of TBHP used corresponded to the same molar concentration values.

Test results for the 2, 6 DMQ/TBHP and DDC/TBHP interactions are given in Tables III and IV, respectively. All of the dopants were added at a concentration equivalent to $3.21 \times 10^{-2}M$. Examination of these results indicates that TBHP had no effect when added as a co-dopant with 2,6-DMQ. The highest amounts of total insolubles were formed in the unvented tests where DDC and TBHP were added with almost a two-fold increase over the vented trials with the same dopants and over the tests where only DDC was present.

Autoxidation of 2-MP, 2,6-DMQ and DDC in the Presence of Organic Acids and Bases

In an extension of our study of interactive effects, two organic acids and two organic bases were examined as co-dopants in fuel D-11. This work was intended to determine whether the autoxidation of the nitrogen compounds is subject to acid or base catalysis. The four co-dopants selected for study were hexanoic acid (HA), dodecylbenzene sulfonic acid (DBSA), tri-n-butylamine (TBA), and 4-dimethylaminopyridine (4-DMAP). All of the dopants were added at a concentration equivalent to $3.21 \times 10^{-2}M$. Accelerated storage stability was assessed at 80°C for 14 days.

With 2-MP, HA and the two bases, TBA and 4-DMAP, showed no effect in the promotion of insolubles. However, the sulfonic acid, DBSA, exhibited a very strong positive interaction in both the vented and unvented tests producing over 700 mg/100 ml of insolubles (Table V). It is reasoned that 2-MP and DBSA form a salt, a polar material which is insoluble in the low polarity fuel.

Results from the interaction studies with 2,6-DMQ are shown in Table III. The two organic bases showed no synergism and HA showed a slight positive interaction producing about 2.0 mg/100 ml of insolubles. The addition of the sulfonic acid, DBSA, caused copious amounts of an opalescent tan solid to form in all the interactive flasks. This solid is very likely the sulfonate salt. There was more than 1000 mg/100 ml but the exact amount was hard to determine because of the difficulty encountered in filtering this solid.

The combination of a carboxylic acid, HA, or a sulfonic acid, DBSA, with DDC results in a strong negative interactive effect with the highest amount of sediment (14.0 mg/100 ml) produced in the vented flask of the HA/DDC interaction. The addition of TBA as a co-dopant with DDC appeared to be synergistic while the addition of 4-DMAP had a negative interactive effect (Table IV).

CONCLUSIONS

The model compound dopant studies show that the pyridine and the quinoline were inactive as sediment producers by themselves and with all co-dopants except a soluble sulfonic acid which interacted to form large amounts of insolubles. DDC formed large amounts of insolubles by itself and exhibited both positive and negative interactions with co-dopants.

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Table I
Total Insolubles for DFM with Added Dodecahydrocarbazole
mg/100 ml**

ppm N (w/v)	Fuel	D-11 80°C 7 days	D-1 80°C 14 days	D-11 43°C 70 days	D-11 43°C 140 days
0		0.2	1.0	-0.4	0.1
45		46.6	38.5	26.1	49.6
45*		42.4	51.7	1.1	6.1
135		75.3	102.7	61.2	88.9
270		158.7	177.2	193.0	128.5
450		322.9	267.8	328.4	244.9
450*		220.8	271.0	99.9	140.8

* Vented

** Averages for duplicates

Table II

Total Insolubles for Stressed DFM with Added 2-MP
and TBHP
(mg/100 ml)

80° - 14 days - D-11 - duplicate tests

<u>Sample #</u>	<u>Total Insoluble</u>
Fuel Blanks	-0.2 0.0
Lo TBHP Blanks	0.0 0.1
Lo TBHP/Lo- 2-MP	0.6 1.0
Lo TBHP/Lo- 2-MP	1.5 0.9
Lo TBHP/H1- 2-MP	0.4 0.3
Lo TBHP/H1- 2-MP	0.6 0.4
H1 TBHP Blanks	0.4 0.2
H1 TBHP/Lo 2-MP	0.5 0.7
H1 TBHP/ Lo 2-MP*	1.8 2.4
H1 TBHP/H1 2-MP	1.3 0.3
H1 TBHP/H1 2-MP*	1.7 1.4

* Flasks Vented

* See Text for Concentrations

Table III

Total Insolubles for stressed DFM with
2,6-DMQ + Various Co-dopants
80°C - 14 days - D-11

Sample #	Total Insolubles, mg/100 mls				
	TBHP	4-DMAP	TBA	HA	DBSA
Blank Fuel	0.2	0.4	-0.1	0.0	0.2
2, 6-DMQ Blanks	0.4	1.5	0.6	0.5	0.3
A-2 Blanks	1.3	0.6	0.4	0.4	1.1
A-2 + 2, 6-DMQ** (unvented)	1.3	0.6	0.2	1.9	>1000.0*
A-2 + 2, 6-DMQ** (vented)	1.5	0.6	0.4	2.1	>1000.0*

* A-2: Co-dopant
Concentration: 3.21×10^{-2} M

* Gravity filtered - Dried - Taken off filter and weighed.

** Average of Triplicates; all others average of duplicates.

Table IV

Total Insolubles for Stressed DFM with DDC +
Various Co-dopants
80°C - 14 days - D-11

Sample #	Total Insolubles, mg/100 mls				
	TBHP	4-DMAP	TBA	HA	DBSA
Blank Fuel	0.0	0.3	0.1	0.0	0.2
DDC Blanks	168.5	262.3	191.8	135.2	258.2
A-2 Blanks	2.8	31.1	4.3	0.0	1.7
A-2 + DDC* (unvented)	310.4	160.8	285.5	2.1	2.3
A-2 + DDC* (vented)	176.4	165.4	291.0	14.0	3.8

* A-2: Co-dopant
Concentration: 3.21×10^{-2} M

* Average of Triplicates; all others average of duplicates.

Table V

Total Insolubles for Stressed DFM with 2-MP
 + Various Co-dopants
 80°C - 14 Days - D-11

Sample #	Total Insolubles, mg/100 mls			
	4-DMAP	TBA	HA	DBSA
Blank Fuel	0.0	0.1	0.0	2.7
2-MP Blanks	0.5	0.3	0.2	1.0
A-2 Blanks	-0.2	-0.2	0.2	0.1
A-2 + 2-MP* (unvented)	0.1	0.0	0.0	757.2
A-2 + 2-MP* (vented)	0.2	0.1	0.0	719.9

* A-2: Co-dopant

Concentration: 3.21×10^{-2} M

* Average of Triplicates; all others average of duplicates.